

New Identification of Metallic Phases of In Atomic layers on Si(111) Surfaces

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We report first-principles calculations that clarify atomic structures and coverage of the metallic phases of In overlayers on Si (111) surfaces. Calculated energy bands and scanning tunneling microscopy images along with the obtained energetics of various phases reveal that the two metallic phases with the $\sqrt{7} \times \sqrt{3}$ periodicity observed experimentally are single and double In overlayers, as opposed to prevailing assignments.

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Surfaces ubiquitous in nature provide new phases of materials due to symmetry breaking and modification of interactions among constituting elements. A thin layer of metallic elements on a semiconductor surface is an example. It offers a good stage to study two-dimensional electron systems (2DESs), and also a key structure in device fabrication in current technology encountered with the cutting-edge miniaturization [1].

Indium adatom layers on Si(111) surfaces are typical and important examples. A particular phase with the lateral periodicity of $\sqrt{7} \times \sqrt{3}$ exhibits metallic behavior down to several K [2], as opposed to the metal-insulator transition predicted for the 2DESs [3, 4], and eventually becomes superconducting at 3 K [5, 6]. This is the first case where superconductivity is found in a deposited layer. Angle-resolved photoemission spectroscopy (ARPES) clarifies the band structure of the metallic phase of the $\sqrt{7} \times \sqrt{3}$ surface [7]. However, atom-scale identification, *i.e.*, the In coverage, the stable atomic structure and the resultant electron states, of the metallic phase is still lacking.

Various surface reconstructions emerge by depositing In atoms on the Si(111) 7×7 surface [8], followed by annealing at ~ 500 °C in ultra-high vacuum: The $\sqrt{3} \times \sqrt{3}$, the $\sqrt{31} \times \sqrt{31}$, and the 4×1 phases appear consecutively with increasing the In dose, all showing insulating behavior at low temperature [9, 10]. Then the $\sqrt{7} \times \sqrt{3}$ phase [11] appears with the In deposition of 1.5 - 1.8 ML. The STM topographs [9, 11] show that the two distinctive structures coexist on the $\sqrt{7} \times \sqrt{3}$ phase: Bright spots appear in a quasi-hexagonal pattern with protruding trimers in one structure (hex structure hereafter), and they appear in a quasi-rectangular pattern in the other structure (rect structure). The former and the latter have been speculated to be 1.0 ML and 1.2 ML, respectively, In adatoms on the Si(111) surface [9, 11]. The excess In atoms are desorbed from the surface in the annealing. The metallic behavior [2, 7] and the superconducting gap [5] have been observed on the rect structure, whereas the metallic behavior and the superconducting current has been measured on the hex structure [6]. Identification of the hex and the rect structures based on the first-principles calculations is highly demanded.

In this Letter, we unequivocally identify the two metallic phases of $\sqrt{7} \times \sqrt{3}$ - In/Si(111) by performing total-energy electronic-structure calculations in the density-functional theory. The obtained energetics, energy bands and scanning tunneling microscopy (STM) images are indicative that the surface measured by ARPES is of the rect structure and is the 2.4 monolayer (ML) In atomic layers, in sharp contrast to the possibilities discussed in the past. The hex structure, on the other hand, is clearly identified as the 1.2 ML In atomic layers. We have found that the both structures are metallic.

Our calculations have been performed with using the local density approximation (LDA) [12] in the density functional theory (DFT) [13, 14]. Norm-conserving pseudopotentials [15, 16] are used to describe the electron-ion interactions. Valence-state Kohn-Sham (KS) wave functions are expanded by a plane-wave basis set with the cut-off energy of 49 Ryd. The In-covered Si(111) surface is simulated by a repeated slab model. Geometry optimization is done until the remaining force on each atom becomes less than 50 meV / Å [17].

We start with the 1.0 ML In on Si(111) in which there are 5 In atoms per $\sqrt{7} \times \sqrt{3}$ lateral cell. This has been postulated to be the hex structure observed by STM. We prepare several initial geometries where In atoms are located at plausible positions in the cell, and perform geometry optimizations. We have then reached the most stable structure in which the $\sqrt{7} \times \sqrt{3}$ periodicity disappears and the 1×1 periodicity comes up instead [Fig. 1(a)]. The next stable structure keeps the $\sqrt{7} \times \sqrt{3}$ periodicity, but its total energy is higher than the most stable structure by 50 meV per 1×1 area. Figure 1(b) shows the energy bands of the most stable structure. Hybridization of In orbitals with Si dangling-bond orbitals leads to a *non*-metallic band structure with the energy gap of ~ 50 meV. The hex surface identified by the STM experiment is known to be metallic, however [6]. We thus conclude that the In 1.0 ML surface is *not* the observed $\sqrt{7} \times \sqrt{3}$ -hex structure.

We next examine the 1.2 ML In on the Si(111), which has been postulated to be the rect structure observed by STM. The number of In atoms is 6 per cell. In the obtained stable geometry, the 3 In atoms are located above

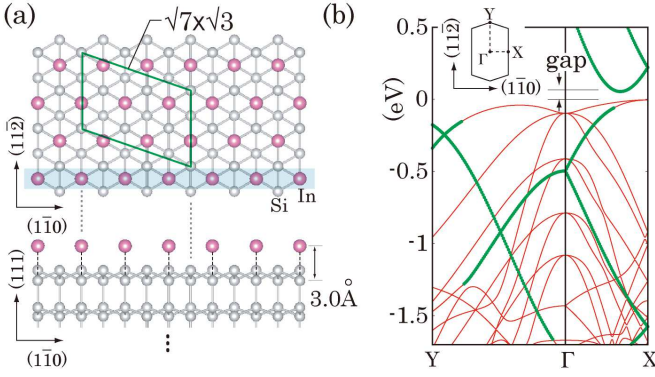


FIG. 1: (color online) (a) Top and side views of the stable structure of the 1.0 ML In surface. Pink (large) and silver (small) balls depict In and Si atoms, respectively. Only the In atoms in the shaded region of the top view are shown in the side view. (b) Band structure with the lateral Brillouin zone corresponding to the $\sqrt{7} \times \sqrt{3}$ lateral cell. The Kohn-Sham (KS) electron states which have the character of In orbitals more than 50 % are depicted by green (bold) lines.

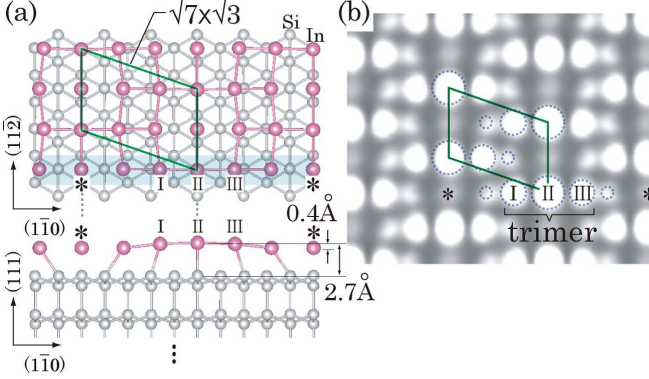


FIG. 2: (color online) Top and side views of the stable structure for the 1.2 ML In surface. Pink (large) and silver (small) balls show In and Si atoms, respectively. (b) Calculated STM image. Dotted circles are guides for eye, showing bright spots. Trimers come from upper In atoms labeled as I, II, and III. The In atoms labeled as * become invisible in the STM image.

the top-layer Si atoms, whereas others lack the partner Si atoms, leading to a corrugation of the In layer as large as 0.4 Å [Fig. 2(a)]. The corrugation is indeed observed by STM for both the hex and the rect structures [11].

Figure 2(b) shows the calculated STM image of the 1.2 ML In on Si(111) [18]. We clearly observe bright trimers which reflect the electron density from the upper 3 In atoms in the corrugated structure. The corrugation also makes certain In atoms, labeled as * in Fig. 2(a) sink to the Si surface and invisible in the STM image. Then the calculated STM image shows 5, *not* 6, bright spots with a prominent trimer in the $\sqrt{7} \times \sqrt{3}$ cell. This feature is exactly what is observed experimentally for the hex structure. We thus naturally conclude that the hex structure is the 1.2 ML In on Si(111), as opposed to the

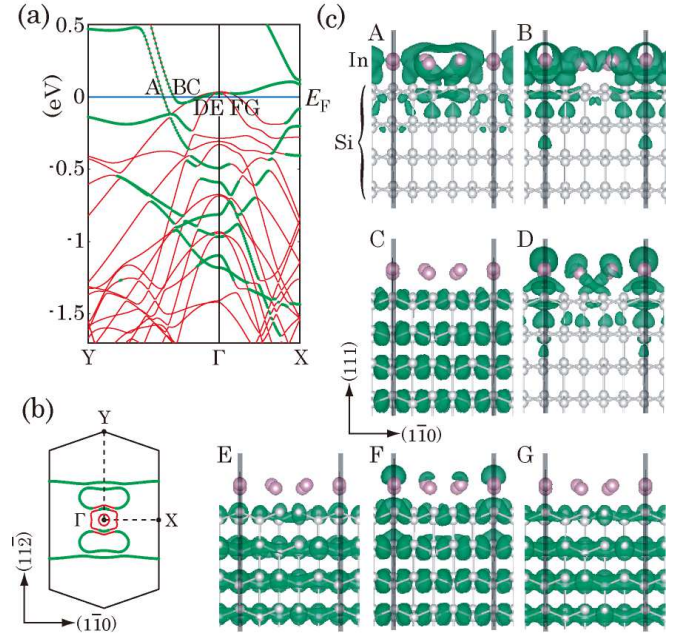


FIG. 3: (color online) Energy bands (a) and Fermi lines (b) of the 1.2 ML In surface. The KS electron states which have the character of In orbitals more than 50 % are depicted by green (bold) lines. The Fermi level E_F is set to be 0. (c) Isosurface of the squared absolute values of the KS orbitals on the Fermi level, at 10 % of the maximum.

previous assignment to the 1.0 ML In on Si(111).

Figure 3 shows calculated energy bands (a) and Fermi lines (b) of the 1.2 ML In surface. We find that the band structure has a metallic character with several bands crossing the Fermi level E_F . Two of them, shown by red (thin) lines in Fig. 3(a), have a character of the top of the Si valence bands, and the others, shown by green (bold) lines in Fig. 3(a), are of In characters. The corresponding wave functions are shown in Fig. 3(c). The calculated energy bands are qualitatively different from those determined by ARPES experiment for the rect structure (Fig. 2(c) in Ref. [7]). This clearly indicates that the rect structure which has been investigated by the ARPES and is also assumed to be responsible for the electron transport at low temperature [2, 5] is *not* the 1.2 ML In on Si(111).

Then, what is the identity of the rect structure? We now argue that it is a double layer In atoms on Si(111) with the coverage of 2.4 ML. Figure 4(a) shows the most stable structure of the 2.4 ML In on Si(111). The number of In atoms per $\sqrt{7} \times \sqrt{3}$ cell is 12, of which 6 are in the top In layer and the other 6 are in the second In layer. This arrangement is akin to that on the (001) face of the body centered tetragonal In crystal. The calculated amount of the corrugation in the top In layer is 0.1 Å, which is substantially smaller than the value calculated for the stable 1.2 ML In structure (0.4 Å). It is of note that, in the STM measurements, the corrugation in the

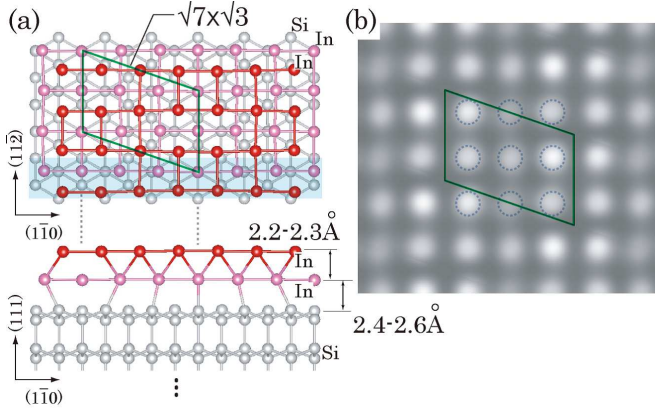


FIG. 4: (color online) (a) Top and side views of the stable structure of 2.4 ML In surface. Red and pink balls are In atoms in the top and the 2nd layers, respectively, and silvers are Si atoms. (b) Calculated STM image. Dotted circles are guides for eyes showing bright spots.

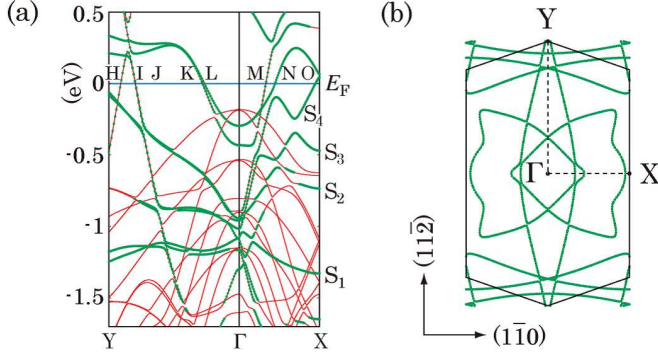


FIG. 5: (color online) Energy bands (a) and Fermi lines (b) of the 2.4 ML In surface. The KS electron states which have the character of In orbitals more than 50 % are depicted by green (bold) lines.

rect structure is smaller than that in the hex structure.

Figure 4(b) is the STM image calculated for the most stable structure of the 2.4 ML In on Si(111). We observe a clear rectangular arrangement of bright spots, which correspond to the positions of the top-layer In atoms. We find that the calculated STM image is essentially identical to the experimental one for the rect structure, which has been incorrectly assigned to the 1.2 ML In on Si(111) in the past.

Figure 5 shows calculated energy bands (a) and Fermi lines (b) for the stable 2.4 ML In surface. Several bands cross the Fermi level E_F , showing a metallic nature. Interestingly, the states at E_F dominantly consist of In orbitals (Fig. 6), inferring that two-dimensional In metal is formed on Si(111). In Fig. 5(b), we find several distinctive Fermi lines: the first line is located near Γ point forming a square shape around Γ ; the second line extends to Γ -Y direction forming a bow shape; the third line is around Y point extending to Γ -X direction; the

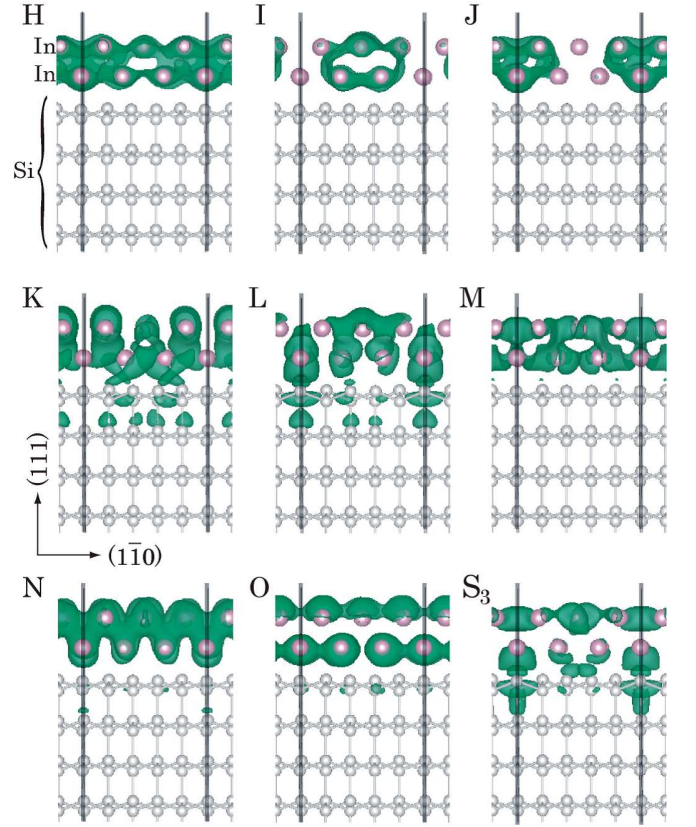


FIG. 6: (color online) Isosurface of the squared absolute values of the KS orbitals on the Fermi level E_F of the 2.4 ML In surface, at 15 % of maximum.

forth line exists around X point extending to Γ -Y direction and forming a butterfly shape.

The presence of the first, the second and the third lines may be understood qualitatively in terms of a two-dimensional nearly-free-electron model [7]. However, the presence of the forth line, or equivalently the presence of S_4 band in Fig. 5(a), is unable to be explained by the simple model. Even for the first, the second and the third lines, the interaction between In and Si orbitals modifies the dispersion of the energy bands substantially. Rotenberg [7] reported ARPES data for the rect structure. The energy bands determined by ARPES show the presence of the nearly-free-electron bands and also other bands which are unable to be explained in the simple model (S_1 , S_2 and S_3 in Fig. 2(c) of Ref. [7]). Our calculations have reproduced these unidentified energy bands, and clarified that they are In states mixed with Si dangling-bond states [see S_3 in Fig. 6]. Agreement of our energy bands and Fermi lines with the experimental ones is excellent [19]. From these electronic structures along with the STM images explained above, we conclude that the observed rect structure is the double-layer In on Si(111) with the coverage of 2.4 ML.

Our argument above is corroborated by the energet-

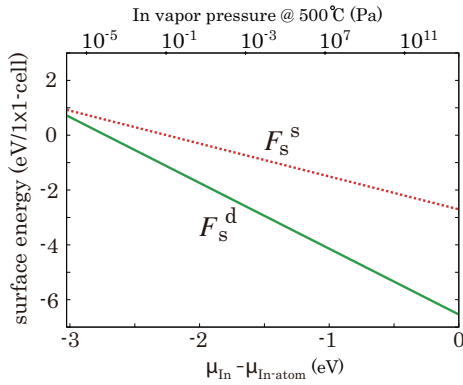


FIG. 7: (color online) Surface energy of a single-layer (1.2ML) In on Si(111), F_s^s , and that of a double-layer (2.4ML) In on Si(111), F_s^d , as a function of the In chemical potential μ_{In} . In vapor pressure at 500 °C corresponding to the value of μ_{In} is also shown.

ics obtained in the present calculations. Figure 7 shows the surface energy defined by $F_s \equiv E_t - F_s^{\text{H}} - \mu_{\text{In}}N_{\text{In}} - \mu_{\text{Si}}N_{\text{Si}} - \mu_{\text{H}}N_{\text{H}}$ as a function of the In chemical potential μ_{In} . Here E_t is the total energy of the slab, F_s^{H} is the surface energy of the H-terminated surface, and μ and N are the chemical potential and the number of atoms in the slab, respectively, of the corresponding elements [20]. We compare the surface energies of the single-layer (1.2 ML) In, F_s^s , and the double-layer (2.4 ML) In, F_s^d . The In chemical potential μ_{In} is taken between the values of the bulk In metal and of the atomic In ($\mu_{\text{In-atom}}$), as the source of In to form the surfaces during the annealing in ultra-high vacuum condition is presumably various In clusters deposited on the Si surface. In case that the surface is in equilibrium with the In gas phase, the In chemical potential is translated to the In pressure at certain temperature, which is also shown in Fig. 7. The result shows that for any value of μ_{In} within this range, the double-layer (2.4 ML) In is energetically favorable. However, in the experiments, the amount of the deposited In is reportedly 1.5 - 1.8 ML when $\sqrt{7} \times \sqrt{3}$ surfaces are made, which is less than 2.4 ML and more than 1.2 ML. Thus, it is expected that obtained surface is a patchwork of the both structures. This corresponds to the observed coexistence of the hex and the rect structures in the experiments [9, 11].

We finally discuss the identity of the superconducting phase. We have revealed that both 1.2 ML and 2.4 ML In-covered surfaces are stable with the $\sqrt{7} \times \sqrt{3}$ periodicity and show the metallic behaviors. The characters of the metallic states are different for the two cases, however: In the 1.2 ML case, both of the Si valence top states and the In orbital states are on the Fermi level [Fig. 3(c)], whereas in the 2.4 ML case the Fermi level states are dominantly of In orbitals (Fig. 6). As for the identification of the superconducting phase, controversial experiments are reported [5, 6]. Considering that the su-

perconducting transition temperature of In layers ($T_c \sim 3$ K) is close to that in the In bulk ($T_c = 3.4$ K), it is likely that the superconducting phase is the rect structure, *i.e.*, the double-layer In on Si(111) with 2.4 ML coverage, in which carriers are dominantly of In character. However, it cannot be excluded that the hex structure becomes superconducting with the transition temperature being accidentally the same as the bulk value.

In conclusion, we have calculated the atomic and electronic structures of the $\sqrt{7} \times \sqrt{3}$ -In/Si(111) surfaces by first-principles calculations based on the DFT. Calculated band dispersions, STM images, and energetics identify the $\sqrt{7} \times \sqrt{3}$ -hex and the $\sqrt{7} \times \sqrt{3}$ -rect surfaces as 1.2 ML In and 2.4 ML In on Si(111), respectively.

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- [18] STM images are simulated by calculating local density of states above the surface [J. Tersoff and D. R. Hamann, Phys. Rev. B **31**, 805 (1985)]. The calculated images are insensitive to the bias voltage.
- [19] Only near-surface states, shown by green (bold) lines in Fig. 5(a-b), are observed in the ARPES experiment [7].
- [20] The surface energy F_s^{H} of the H-terminated Si (111) is estimated by using the 16-layer Si slab with the bottom and the top surfaces terminated by H atoms. Since the numbers of Si and H atoms in this slab are twice of the corresponding numbers in the slab used in this work, we obtain $F_s^{\text{H}} = E'_t/2 - \mu_{\text{Si}}N_{\text{Si}} - \mu_{\text{H}}N_{\text{H}}$ with E'_t being the total energy of the 16-layer slab.